Polymer Degradation and Stability 96 (2011) 51–59

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

A study on the dispersion, preparation, characterization and photo-degradation of polypropylene traced with rare earth oxides

Feliks Bezati [a,c,*], Valérie Massardier [a], Jean Balcaen [b], Daniel Froelich [c]

[a] *Ingénierie des Matériaux Polymères - Laboratoire des Matériaux Macromoléculaires (IMP/LMM), UMR-CNRS 5223, INSA-Lyon, 17 avenue Jean Capelle, F-69621 Villeurbanne Cedex, France*

[b] *Site de Plasturgie-IMP/LMM, UMR-CNRS 5223, 6 rue Pierre et Marie Curie, F-01108 Oyonnax, France*

[c] *Laboratoire Conception Produit Innovation, Chambéry (LCPI), Institut ARTS et METIERS ParisTech Chambéry, Savoie Technolac, 4 Rue du Lac Majeur, F-73375 Le Bourget du Lac Cedex, France*

ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form
18 October 2010
Accepted 9 November 2010
Available online 8 December 2010

Keywords:
Polyolefin
Rare earth oxides
Tracer
Mechanical properties
Photo-degradation

ABSTRACT

This research work deals with the effect of rare earth oxides on the PP matrix with respect to the thermal and mechanical properties and to the photo-degradation under UV irradiation exposure. The rare earth oxides are used as tracers for the identification of polymer materials, in order to have an economically efficient recycling and high speed automatic sorting of plastic wastes. The addition of 0.1 wt% of such particles of a micrometric size has a minor effect on the mechanical and thermal properties of the traced materials, as well as on the photo-degradation of the polymer after UV irradiation exposure. For 1 wt% tracer content, before UV irradiation treatment, the melting and crystallization temperatures as well as the thermal stability of the PP matrix are slightly increased, whereas the elongation at break decreases from 10 to 50% for a cross-head speed of 250 mm/min. However, the addition of 1 wt% of CeO_2 improves the photo-degradation resistance of the PP matrix to UV exposure due to the UV light screening effects offered by these particles. The SEM images together with the results obtained from image processing show a homogenous dispersion of tracers in the PP matrix.

1. Introduction

Tracers consist of systems formed by one or several substances dispersed into a material with the aim of adding a selective property to it and improving its identification. In recent works [1,2], an X-ray fluorescence (XRF) detection system based on the use of tracers for the identification of polymer materials was reported by the authors. This system was developed with the objective of having an economical, efficient and automatic sorting of plastic wastes. The addition of X-ray fluorescent tracers in polymer materials during the compounding process, offers many benefits by increasing the efficiency and purity of sorting and providing a solution for the identification of dark plastics.

Tracers must not chemically react with the host material, and cause changes to any of their physical, chemical or mechanical properties beyond acceptable limits. For products which are likely to have long useful lives under normal outdoor environment, such as automotive parts, the tracer particles need to be highly stable under weathering and during plastic processing [3].

The automotive and electrical industries are currently the worst performers concerning the recycling of plastics. This is partly due to the complexity of the waste materials that these sectors produce [4]. For this study, polypropylene (PP), one of the world's major plastics, abundantly present in polymers to be recycled from the End of Life Vehicles (ELV) and the Waste of Electric and Electronic Equipments (WEEE) was chosen.

XRF is a volume, non-destructive spectroscopic method enabling elemental analysis of materials. Therefore the choice of tracers is directly linked to the elements of the periodic table. Once the toxic and radioactive elements are eliminated, along with the elements present in polymer additives, the low atomic number elements and the elements with limited reserves, the result leads to the selection of rare earth elements. For these selected ones we have chosen the most stable chemical molecules, the oxides [5]. The rare earth oxides (Y_2O_3, CeO_2, Nd_2O_3, Gd_2O_3, Dy_2O_3, Er_2O_3 and Yb_2O_3) used for this study are neither abrasive, nor toxic during their application and use and also stable in the environment [6,7].

The minerals used as fillers in polypropylene are principally talc and calcium carbonate. However, little attention has been paid to

---

[*] Corresponding author. Ingénierie des Matériaux Polymères - Laboratoire des Matériaux Macromoléculaires (IMP/LMM) UMR-CNRS 5223, INSA-Lyon 17 avenue Jean Capelle, F-69621 Villeurbanne Cedex, France. Tel.: +33 (0) 472 436 003; fax: + 33 (0) 472 438 527.

E-mail address: feliks.bezati@insa-lyon.fr (F. Bezati).

0141-3910/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2010.11.008

Table 1
Materials specifications.

Materials	Chemical name	Supplier	Particles' size (μm)
PP	Polypropylene	REPSOL	2000
Y_2O_3	Yttrium oxide	RHODIA	2.250
CeO_2	Cerium oxide	RHODIA	2.250
Nd_2O_3	Neodymium oxide	AMPERE	3.500
Gd_2O_3	Gadolinium oxide	RHODIA	1.850
Dy_2O_3	Dysprosium oxide	RHODIA	2.250
Er_2O_3	Erbium oxide	AMPERE	8.200
Yb_2O_3	Ytterbium oxide	AMPERE	1.000

rare earth compounds used as fillers in polymers. As rare earth minerals are abundant in China, some studies investigating polypropylene composites containing rare earth oxides were published by Chinese scientific committees. Liu et al. [8,9] have studied the effect of a large number of rare earth oxides on isothermal crystallization and melting behaviour with differential scanning calorimetry. They found that a series of rare earth oxides in a fine powder form may act as a nucleating agent and influence the growth rate of the spherulite and the mechanical properties of polypropylene. Other studies of Xiaomin et al. [10] have shown that the addition of Y_2O_3 has some effect on the viscosity of the system. Crystallization characteristics have indicated that the filler acts as a nucleating agent, increasing crystallization rate of the investigated polymer, and changing β crystal form content.

Regarding the effect of rare earth oxides in photo-degradation, cerium oxide (CeO_2) nanoparticles are used in wood coating technologies as UV absorbers [11], as they show a UV cut-off threshold at around 370 nm, similar to that of titanium oxide. The use of fine particles of cerium oxide has also been mentioned as an effective inorganic sunscreen for personal care products for replacing titanium and zinc oxides [12]. Tessier et al. [13] have studied Y/Ce substitution of ceria in order to shift efficiently the absorption edge towards the UV/Vis transition (400 nm). They have concluded that the compositions proposed are interesting for UV absorbers applications for the wood industry. Moreover, the use of Yttrium oxide (Y_2O_3) was mentioned in literature for its application as a protector of aluminium and silver mirror coatings, due to its capacity to absorb widely in the near-UV spectrum (300 nm) [14,15].

Following the above mentioned previous works [1,2], which report the possibility of detecting rare earth oxides through the use of XRF, our study presents a complementary approach with a research on the dispersion, elaboration, characterization and photo-degradation of traced polypropylene with rare earth oxides. The main objectives of this study are first, to quantitatively characterize the dispersion of tracers in the PP matrix which is of prime importance for their detection and for the mechanical properties of the traced PP. Second, to study the effect of tracers as fillers in the PP matrix with respect to the thermal and mechanical properties and to the photo-degradation under UV irradiation exposure. Third, to finally estimate the tracer concentration for which the properties of the polymer matrix will not be affected.

2. Experimental

2.1. Materials and preparation of traced polypropylene composites

The investigation described in this paper was conducted with a commercial grade of isotactic polypropylene homopolymer (ISPLEN PP 050 G1E) manufactured by Repsol. The original pellets have a melt mass-flow rate of 5.8 g/10 min (2.16 kg at 230 °C) and a density of 0.905 g/cm^3. ISPLEN PP 050 G1E is intended for applications that require good impact resistance and is believed to contain low quantities of UV stabilizers and a small amount of heat stabilizer in order to minimize degradation during processing.

The characteristics of the rare earth oxides used as tracers are given in Table 1. The tracer content in the composites is 0.1 and 1%, respectively. All traced materials were prepared under identical mixing and moulding conditions. The injection moulded specimens of 2 mm thickness were produced by using a Battenfeld Unilog B2/350 Plus injection moulding machine. The barrel temperature was fixed at 220 °C for all zones. Before being injected the pellets were extruded twice by using a twin screw extruder CLEXTRAL BC21 machine (screw of $L/D = 90$ and $D = 25$ mm) for dispersing homogenously the tracers in the PP matrix. The extrusion temperature, the screw speed and the residence time were 205 °C, 120 rpm and 15 min, respectively. The screw and temperature profiles used in this study are supplied in Fig. 1.

For PP containing 0, 0.1 and 1 wt% of tracers (T), the materials will be designed as PP, PP_T_0.1 and PP_T_1, respectively. For the samples subjected to UV irradiation treatment, they will be referred to as UV-PP, UV-PP_T_0.1 and UV-PP_T_1, respectively.

All samples were kept for at least 1 month at room temperature before undergoing UV exposure in order to ensure that they had reached a near-equilibrium state, following ageing due to post-moulding effects such as secondary crystallization.

2.2. Microscopic observation

The tracers and their dispersion in the PP matrix were observed by Scanning Electron Microscopy (SEM) using a Hitachi S3500N model. The specimens prepared by injection moulding were fractured in liquid nitrogen and sputter-coated with gold before being examined with the microscope at an accelerating voltage of 30 kV. The SEM images were analysed by MATLAB by applying image processing.

2.3. UV irradiation procedure

UV irradiation treatment for the injection moulded specimens were carried out using a QUV accelerated weathering machine (QUV Solar Eye), with a light intensity of 0.68 W/m^2. The source of UV radiation was fluorescent tubes UVA-340, which have an output matching reasonably close to the solar radiation in the UV range [16]. The surface of the samples was subjected to a cycle of 4 h of UV irradiation at 60 °C and 4 h of condensation at 50 °C. The total exposure time of specimens was 2160 h (3 months).

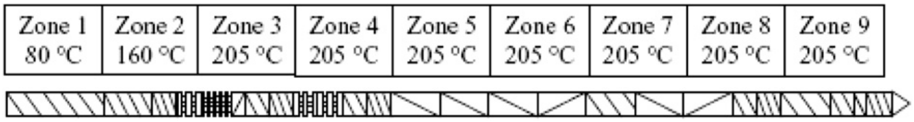

Fig. 1. Screw and temperature profiles for the extrusion processing.